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Thermodynamic and structural properties of water adsorbed film on MgO (100) ionic surface

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Abstract We have investigated by adsorption isotherms and neutron diffraction measurements, respectively the thermodynamic and structural properties of water physisorbed film on MgO (100) powder. Thanks to a high temperature thermal treatment, under vacuum, our MgO powder samples are characterized by a highly homogeneous (100) MgO surface. We have determined the structure of the (2D) water film physisorbed on such an ionic surface. This one is a commensurate P(2×3) structure which is very similar to the (110) planes of ice-VII. Recall that ice VII, which is stable at very high pressure, is characterized by a quite large density (d = 1.6).

Keywords Water physisorption · MgO (100) powder · Adsorption isotherms · Neutron diffraction · P(2×3)commensurate structure · Ice-VII · (2D) High density water solid phase

1 Introduction

High homogeneous MgO (100) powder is a very suited substrate to investigate the effect of square symmetry surface on the structural properties of physisorbed (2D) films. It is interesting to make a comparison with the structural properties of such (2D) films physisorbed on the so-called graphite (001) surface of hexagonal symmetry (Coulomb and Vilches 1984; Coulomb et al. 1984, 1985). Indeed, the natural organization of (2D) films, composed of rare gases or globular molecules, is the hexagonal close packed (hcp) structure. As a consequence, the square symmetry of the adsorption sites of the MgO (100) surface induces some frustration in the hcp (2D) crystallization phenomenon (Ferry et al. 1996, 1997). Moreover, the MgO (100) surface is of great interest to analyse the effect of the surface electric field E, on polar adsorbed (2D) films [as for example, N_2, CO or C_2H_2 monolayer (Madih et al. 1989; Trabelsi et al. 1991; Trabelsi and Coulomb 1992; Coulomb et al. 1994)]. Roughly speaking, in addition to an usual "positional" commensurability, surface electric field E induces an "orientational" commensurability. When both MgO surface effects exist, as for acetylene molecules, large retarding effects on the (2D) melting are observed [the (2D) triple point temperature T_{2t} is larger than the bulk one, $T_{2t} > T_{3t}$ (Coulomb et al. 2012)].

In the present study we want to investigate these two types of MgO (100) surface effects on the water physisorbed film properties. Indeed, contrarily to graphite (001) surface which is not wet by a water monolayer, a physisorbed water (2D) film is observed on the (100) MgO surface (as represented in Fig. 1). The adsorbed water monolayer on MgO (100) surface system has been the topic of important experimental and theoretical attention (Heidberg et al. 1995; Ferry et al. 1998; Demirdjian 2000; Giordano et al. 1998; Foster et al. 2002; Finocchi et al. 2008). The recent paper of Wlodarczyk et al. (2011) summarizes in a clever way the (2D) phase diagram properties of such a system. Two water structures, characterized by the C(2×4) and the P(2×3) commensurabilities, are stable below and above 185 K, respectively. Nevertheless, the position and the orientation of the water molecules in these two commensurate meshes are not

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determined. Our paper is the first one which gives reliable answer to the P(2×3) structure determination. We have studied the thermodynamic and structural properties of the (2D) water film physisorbed on MgO (100) surface. Some interesting results concern also the H-bonding formation within the water monolayer and between the monolayer and the surface oxygen ions of the MgO substrate. In parallel to the water/MgO physisorbed system, we also have explored water sorption in mesoporous silica of the MCM-41 type and in microporous model alumino-phosphate as $AlPO_4$-5 (Llewellyn et al. 1996; Coulomb et al. 1998; Floquet et al. 2004, 2005). Note that neutron diffractogram of (2D) physisorbed water phase on MgO (100) surface is quite different from diffractograms of the bulk water (liquid and hcp ice phases) or of the confined quasi-(1D) water (as shown in Fig. 2).

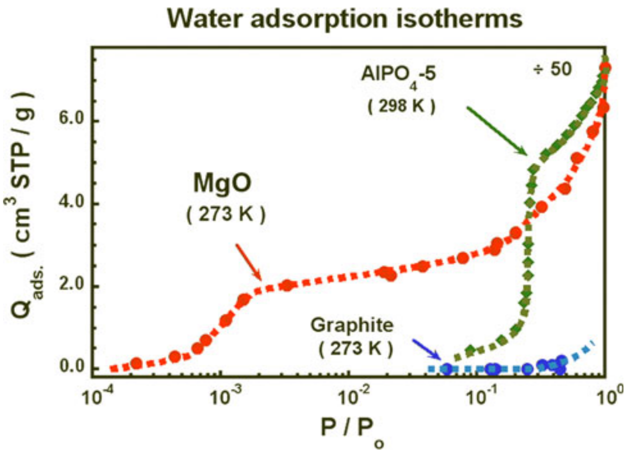

Fig. 1 Adsorption isotherm of water on MgO (100) powder measured at T = 273 K. By comparison, water adsorption isotherms, on $AlPO_4$-5 model zeolite and on graphite (001) measured at 298 and 273 K respectively, are represented

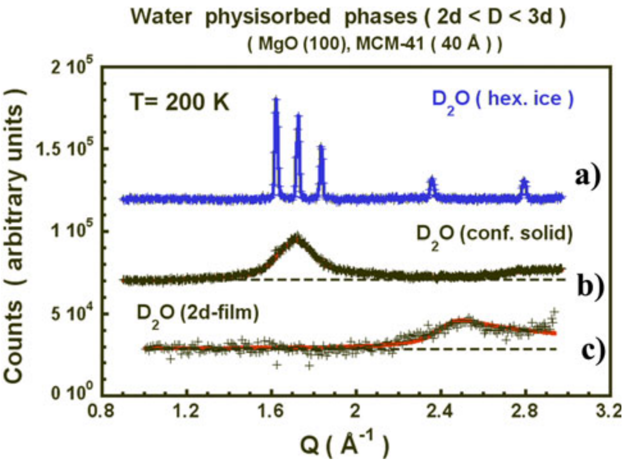

Fig. 2 Neutron diffractograms measured at 200 K on: (*a*) (3D) hexagonal ice; (*b*) confined water on MCM-41 (40 Å) and (*c*) water physisorbed (2D) film on MgO (100) powder

2 Experimental section

Our MgO powder samples were prepared by a method described in detail in the reference (Coulomb and Vilches 1984). Magnesium ribbons were burned in dry atmosphere. The MgO smoke was collected and outgassed under vacuum ($P \leq 10^{-6}$ Torr) during around 12 h at T = 950 °C. The samples were transferred in stainless steel sample holders and stored under vacuum. Prior to adsorption isotherm measurements or neutron scattering counts, the MgO powder samples, again were outgassed a few hours at 950 °C. As illustrated in Fig. 3, our MgO samples are composed of perfect crystallized nano-cubes. Such MgO powders produce nice stepped methane adsorption isotherms as represented in Fig. 4. On the same sample we have measured a water adsorption isotherm at T = 273 K. Only one step is observed and in place of the expected isotherm plateau a slight uphill part is observed. As a consequence, it is not easy to determine when the coverage value equals a full monolayer. We choose rather arbitrarily the central point of the isotherm "false plateau" as coverage equal to one layer, as shown in Fig. 4. That point corresponds roughly to a methane bi-layer physisorbed quantity. Hence, we can conjecture that the water (2D) film density should be significantly higher than the commensurate C(2×2) methane structure (Coulomb et al. 1985).

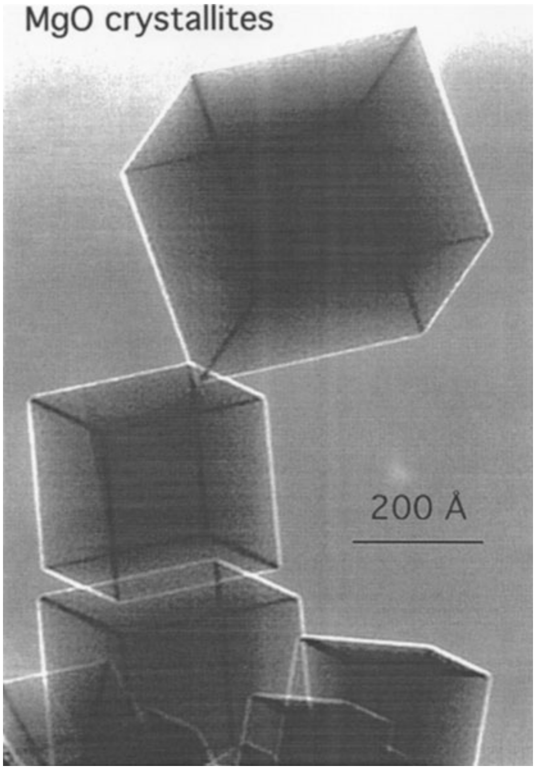

Fig. 3 Transmission electron micrograph of our MgO powder sample, which is mainly composed of well defined nano cubes

3 Results and discussion

We have measured the neutron diffractograms of water (D_2O) phase adsorbed on MgO (100) surface at different film thicknesses (0.93; 1.5; "4.0" and "20 layers", as represented in Figs. 5, 6). A water (D_2O) calibration adsorption isotherm was measured at T = 273 K, during the neutron diffraction experiment, to determine with high accuracy Q_{ads}. (the water adsorbed quantities, as shown in Fig. 7). We have to note that "4.0 layers" and "20 layers", mean water quantities equal 4 times and 20 times, respectively the water quantity which corresponds to a water monolayer (i.e. 15 cm^3 STP, is defined in Fig. 4). The equilibrium pressures of these points on the adsorption isotherm are equal to the water (D_2O) vapour pressure P_0 at T = 273 K (P_0 = 3.75 Torr).

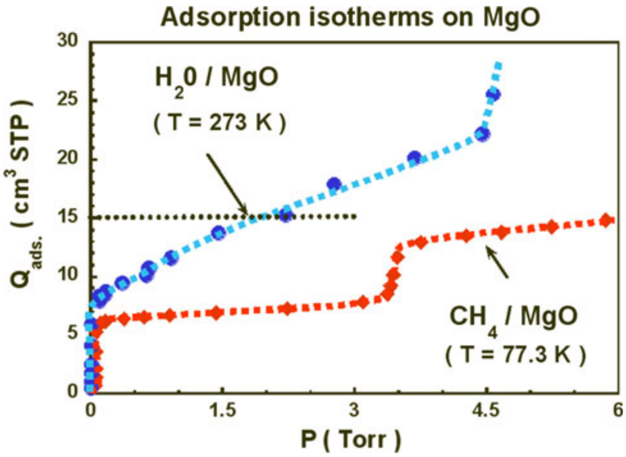

Fig. 4 Calibration adsorption isotherm of highly pure water (H_2O) on MgO (100) powder measured at T = 273 K. By comparison, on the same MgO sample we have measured, a methane adsorption isotherm, at T = 77.3 K

The water neutron diffractogram measured at 273 K, which corresponds to a D_2O quantity equivalent to "20 layers", is characterized by a large diffraction bump located around the wave vector Q value (Q = 1.95 Å^{-1}). Such a diffraction profile is characteristic of the water liquid phase (it reflects the short range order of the water molecular organization). By comparison, neutron diffractogram of the D_2O hexagonal ice measured at T = 200 K is represented in Fig. 2 (a series of narrow diffraction peaks is observed, signature of long range order which characterizes a crystalline molecular organization of the water phase). We have interpreted the neutron diffractogram measured for a physisorbed water quantity equivalent to "4 layers", as corresponding to a mixture of two water phases; a bulk water liquid phase and a (2D) water physisorbed phase on the MgO (100) surface (a decomposition of the neutron diffractogram signal in two parts is illustrated in Fig. 5). The neutron diffraction signal attributed to the water (2D) physisorbed film appears as a diffraction bump located at around the Q value equal to 2.5 Å^{-1}. As we have already mentioned in Fig. 2, the diffraction signal is quite unusual in such a wave vector Q range. We note also that the diffraction signal is rather broad, but it is usual, concerning diffraction from low dimensionality systems LDS (an example of broad diffraction peak from LDS is illustrated by the neutron diffractogram of the water solid confined phase in MCM-41 sample at T = 200 K, as shown in Fig. 2).

The determination of the water monolayer structure was not simple. It was based on the analysis of the 0.93 layer or 1.5 layer diffractograms (as represented in Figs. 5, 6). From an experimental point of view, the water physisorption is not easily controlled. We need to prevent if possible or to

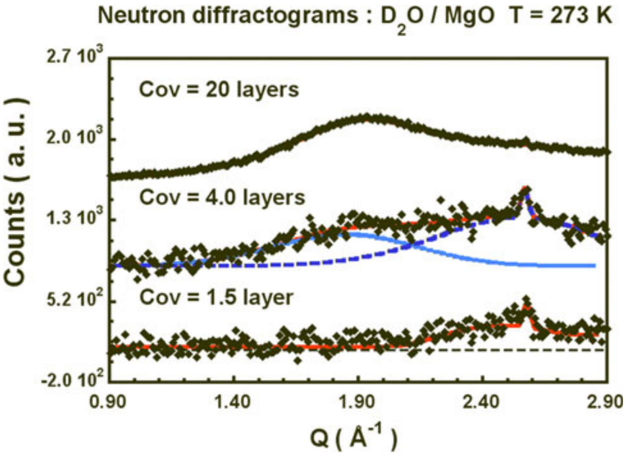

Fig. 5 Neutron diffractograms of D_2O physisorbed films on MgO (100) surface of different thicknesses: 1.5 layer; 4 layers and 20 layers at T = 273 K

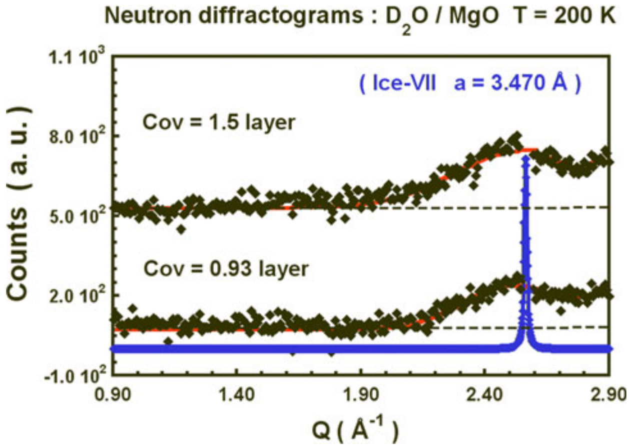

Fig. 6 Neutron diffractograms of D_2O films adsorbed on MgO (100) surface measured at 200 K for coverage 0.93 and 1.5 layer respectively. By comparison the diffractogram of ice-VII is also represented

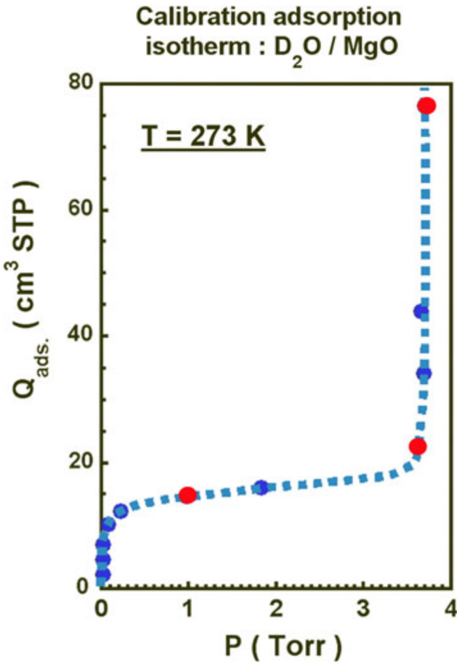

Fig. 7 Calibration adsorption isotherm of heavy water (D_2O) on MgO (100) powder measured at T = 273 K

minimize water adsorption on the different parts of the volumetric adsorption apparatus. A careful comparison with water adsorption results, obtained by gravimetric measurements, has been performed. Three neutron scattering experiments on different diffractometers (both at the LLB Saclay-France and ILL-France, laboratories) have been performed. All the results are in accordance (as illustrated in Fig. 5 results from G4-1 LLB and in Fig. 6 results from ILL).

The first time, we started our analysis by considering water (2D) structure similar to the densest plane of hexagonal ice (Ih) and cubic ice (Ic). The comparison of the diffractograms was not at all significant. The second time, we considered the high density ice structures (ices which exist in the high pressure range). It took time, but after a while, we remarked that the main neutron diffraction peak of the cubic ice-VII and the main peak of our 0.93 layer or 1.5 layer diffractograms were very close to each other, despite their broadness difference (as show in Fig. 6). Moreover, surprisingly, the densest plane of ice-VII (plane (110)), represented in Fig. 8, was very close to the P(2×3) commensurate structure. Structure that we have already conjectured the existence for the water (2D) film (Demirdjian et al. 2000). One remarkable characteristic of such (110) planes is that they are composed of water molecules rows. Along the row, the stability is insured by H-bonding (O–H···O which is the major part of the water molecular interactions), in the (110) plane the interactions between rows are of the van der Waals type. The stability of the whole ice-VII structure results from the H-bonding between the planes. Such dense (110) planes of the cubic ice-VII match very well the P(2×3) commensurate structure of the (100) MgO surface as illustrated in Fig. 9 (the parametric difference is equal to few percents).

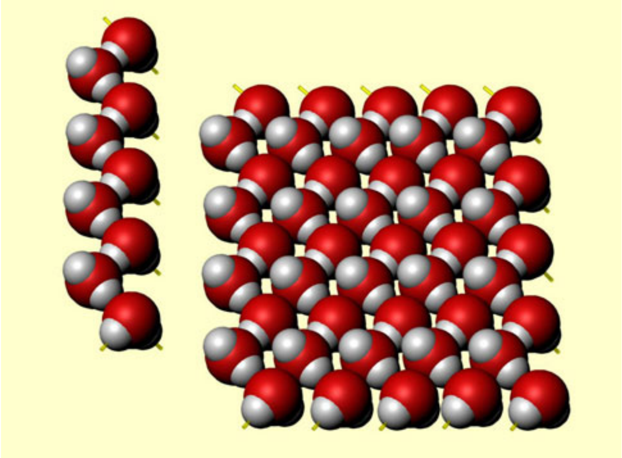

Fig. 8 Schematic representation of the densest plane (110) of ice-VII. Such planes are composed of D_2O chains. H-bonding between the planes insures the stability of ice-VII structure

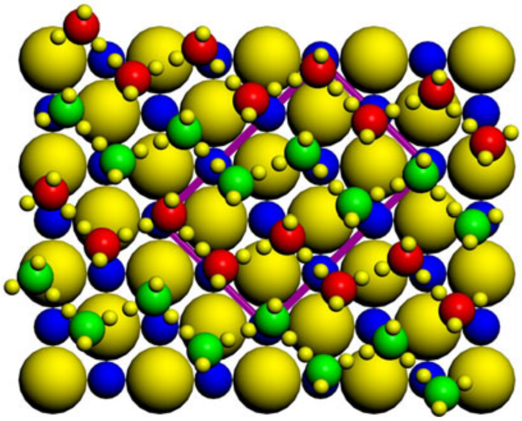

Fig. 9 Schematic representation of one (110) dense plane of the ice-VII structure adsorbed on the MgO (100) surface. Such (2D) water structure, composed of H_2O rows, matches quite well the P(2×3) commensurate structure

Consequently, we decided to calculate the neutron diffractogram of the P(2×3) water monolayer structure considering the chain morphology as D_2O molecular organization within the P(2×3) commensurate mesh. It is quite interesting to note that in such a (2D) chain morphology, all the water molecules are laying down along the surface channels formed by the Mg^{2+} cations (as represented schematically in Fig. 10). For the first time, the calculated neutron diffractogram reproduces the main characteristics of the measured one. Nevertheless, some extra diffraction peaks exist in our calculated model. It was obvious that owing to the H_2O molecular geometry, the

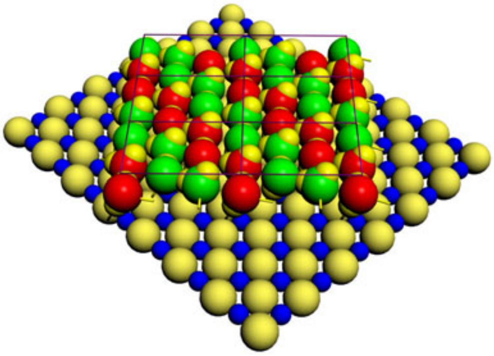

Fig. 10 Schematic representation of the commensurate P (2×3) structure of water monolayer adsorbed on the MgO (100) surface. We note that all the H_2O molecules are laying down along the surface rows formed by the Mg^{2+} cations. Conjectured H-bondings have been also represented

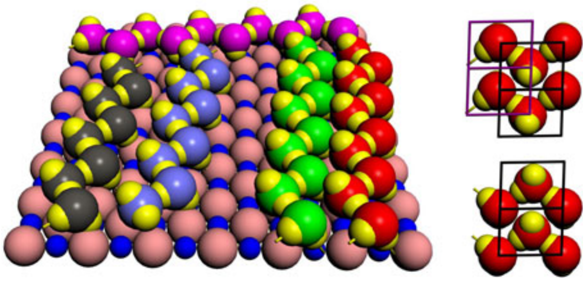

Fig. 11 The water P(2×3) commensurate mesh contains six D_2O molecules. In such a large mesh, the water chains can present a large number N of different morphologies (N = 12). We have to take into account such a disorder to fit our experimental diffractograms

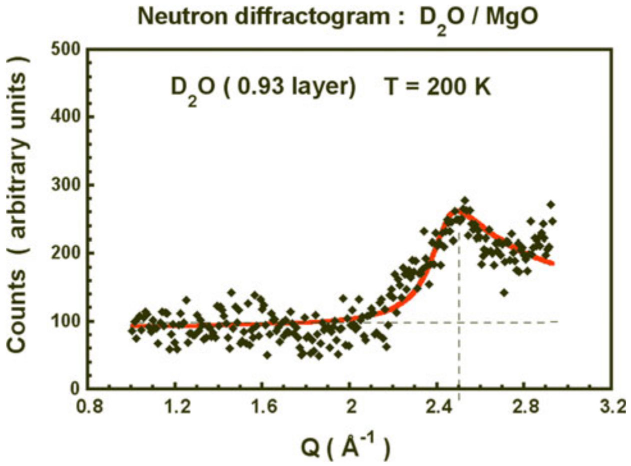

Fig. 12 Neutron diffractogram of D_2O monolayer adsorbed on MgO (100) surface measured at 200 K for a coverage equal to 0.93 layer. The continue *red line* represents the fit obtained by least square adjustment with our calculated neutron diffractogram from the P(2×3) structure including the disorder between the chains (Color figure online)

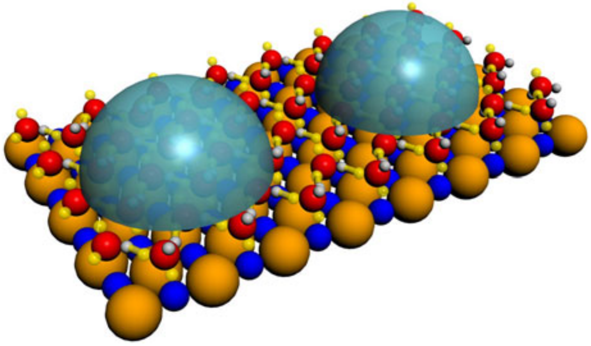

Fig. 13 Schematic representation of the commensurate P (2×3) structure of water monolayer adsorbed on the MgO (100) surface, plus a bulk liquid water phase on top of the water (2D) phase

water chains could adopt different configurations and in addition several sub-lattices could be build from the P(2×3) commensurate structure (in fact 6 sub-lattices). We have to consider these two types of disorders in our calculated diffractograms (different water chain morphologies are illustrated in Fig. 11). We have to emphasize the (1D) character of the water chains. When the water monolayer grows up, we think that individual chain develops first, giving rise to large disorder between the chains. Roughly speaking such a commensurate P(2×3) chains assembly is characterized by a long range order along the chains direction and a short range order in the perpendicular direction. We have introduced the disorders by averaging the calculated neutron diffractograms to all the water chains morphologies (6 sub-lattices plus 2 chains configurations). The results are shown in Fig. 12 concerning the measured diffractogram at T = 200 K for a coverage 0.93 layer. The continuous red line represents our calculated diffractogram obtained by least square adjustment (three parameters are deduced; the position, the broadness and the intensity of the neutron diffraction peak). The same calculation has been performed for the neutron diffractogram measured at the same temperature (200 K) but at higher coverage, 1.5 layer (as shown in Fig. 6). Despite the difference in coverage values, the two neutron diffractograms are very similar. Probably some contribution of bulk water liquid phase exists already for the coverage 1.5 layer. At higher coverage "4 layers" as we have already mentioned we have observed a coexistence of phases between the (2D) P(2×3) water solid phase and a bulk water liquid phase (as depicted in Fig. 5). Such phase coexistence is illustrated in Fig. 13. We have begun to investigate the temperature range of existence of the (2D) P(2×3) water solid phase. It seems that such a domain is rather large from 150 to 273 K considering the measured neutron diffractograms characteristics as described in Fig. 14. We plan to study in more detail the melting of the P(2×3) water structure.

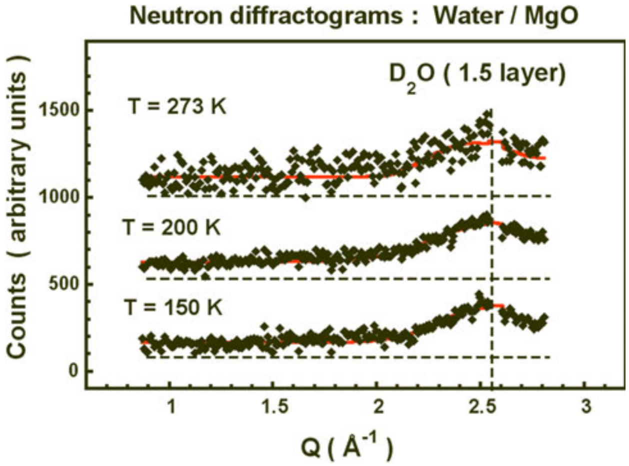

Fig. 14 Neutron diffractograms of D_2O monolayer adsorbed on MgO (100) surface measured at different temperatures (150; 200; and 273 K) for a coverage equal to 1.5 layer

4 Conclusion

In the present paper, we have confirmed the P(2×3) commensurate structure existence and finally we have determined the position and the orientation of the water molecules within the P(2×3) mesh. The principal characteristic of such a (2D) water structural organization is that the D_2O molecules form "zigzag" chains along the MgO (100) surface channels, consequently the water monolayer presents an original and pronounced (1D) nature. Another characteristic of the P(2×3) water structure concerns its quite high density [six molecules in the P(2×3) mesh], twice as big as the methane one. This structural result is in agreement with the measured physisorbed H_2O quantity (as represented in Fig. 4). These observations attest of the great effect of the MgO (100) surface on the structural organization of the physisorbed water (2D) film. The molecular arrangement is quite similar to the high density ice-VII one ($d = 1.6$). It is a nice illustration of the large MgO (100) surface effect. Effect which can be compared to the high pressure values needed to stabilize ice-VII ($P = 2.4$ GPa). We note that the MgO surface effect is limited to the first water monolayer, for thicker films the water structure switch to usual bulk structures (hexagonal ice and liquid water phase). Finally one interesting factor to investigate is the H-bonding interaction between the water monolayer and the O^{2-} MgO surface anions. We think that the position and the orientation of the D_2O molecules that we propose in our paper are geometrically favourable to H-bonding interaction between the MgO substrate and adsorbed water solid phase. We hope that we will motivate infrared experimental investigation for example.

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